Microwave-absorbing characteristics for the composites of thermal-plastic polyurethane (TPU)-bonded NiZn-ferrites prepared by combustion synthesis method

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Abstract

NiZn ferrite with the chemical formula Ni_{0.5-x}Zn_{0.5-x}M_{2x}Fe_{2}O_{4} (M = Co, Cu, or Mg, and x = 0 or 0.05) was synthesized by a combustion synthesis method using metal nitrates and urea ((NH₂)₂CO) as reactants. The nanocrystalline of these materials were mixed with a thermal-plastic polyurethane (TPU) elastomer to be converted into a microwave-absorbing composite. The complex relative permittivity (ε₁ = ε′ − jε″) and permeability (μ₁ = μ′ − jμ″) of the absorber were measured in a frequency range of 2–12 GHz. The reflection loss (R.L.), matching frequency (f_m) and matching thickness (d_m) were calculated using the theory of the absorbing wall. Effects of both the particle size of ferrite and the dopant presented in the ferrite on the electromagnetic properties and microwave-absorbing characteristics were investigated. It was found that nanoparticles around 40 nm exhibit higher reflection loss than both those obtained from micro-sized powders and those with size less than 25 nm. Also, it was shown that the Co-doped, Mg-doped, and Cu-doped NiZn ferrite-TPU composites could be designed to be more negative than −20 dB, in a frequency range of 2–12 GHz, to become promising materials for microwave-absorbing application. These doped ferrite-containing composites have more effective microwave-absorbing characteristics compared to undoped one.

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1. Introduction

Much attention has been attracted by microwave-absorbing materials due to the facts that they can absorb energy from microwave and that they can be widely used in the stealth technology of aircraft, television image interference, and new absorption materials [3–5]. One criterion in selecting the absorbing material is to discover the location of its natural resonance region. Thus, a study of the frequency dependencies of the complex relative permittivity (ε₁ = ε′ − jε″) and permeability (μ₁ = μ′ − jμ″) on the absorbing material has been a field of interest.

In the past, the spinel ferrites have been utilized as absorbing materials in various forms for many years. Also, the ferrite-polymer composites are useful as absorbers due to their lightweight, low cost, and good design flexibility [1,5,6]. Among the spinel ferrites, NiZn ferrites are commercially used as electromagnetic devices operated in high frequencies (>10 MHz), arising from the fact that metal dopants can be used to modify the electromagnetic properties of NiZn ferrites by increasing the resistivity and permeability [7]. For this purpose, some attempts were made to verify the correlation between the material constants, ε₁ and μ₁, and microwave absorption in the sintered ferrites that contain divalent metal ions [6–9].

Recently, the research pursuing to nanocrystalline materials and their properties has been given much attention.
and it is well known that nano-scale particles possess distinctive physical and chemical properties because of their nano-sized crystallite, large surface area and different surface properties (such as surface defect) etc. Yet, a variety of wet-chemical methods (such as sol–gel, co-precipitation and hydrothermal, etc.) have been reported to be effective in generating nano-sized and homogeneous powders of ceramic oxides [10–12]. However, relatively complex schedules, expensive precursors, and low production rate are the common problems of the wet-chemical method [13]. In the past decade, a solution combustion method has been narrated and utilized to synthesize simple and/or mixed metal oxides [14–17]. With this method, the heating and evaporation of desired metal nitrate solution employing an organic compound can result in self-firing to generate heat by exothermic reaction. This liberated heat is used to synthesize the ceramic oxide powders. Together, this method has advantages of applying inexpensive raw materials and maintaining a relatively straightforward preparation process, and achieving a fine powder with high homogeneity. In addition, the process of combustion reaction is relatively quick as compared to other synthesis techniques. This process with its fast pace in ascending and descending the temperature can produce meta-stable phase, un-equilibrium phase and products of tiny grains; therefore, superior properties are attainable compared to other synthesis techniques. This process with its fast pace in ascending and descending the temperature can produce meta-stable phase, un-equilibrium phase and products of tiny grains; therefore, superior properties are attainable compared to other synthesis techniques. This process with its fast pace in ascending and descending the temperature can produce meta-stable phase, un-equilibrium phase and products of tiny grains; therefore, superior properties are attainable compared to other synthesis techniques. This process with its fast pace in ascending and descending the temperature can produce meta-stable phase, un-equilibrium phase and products of tiny grains; therefore, superior properties are attainable compared to other synthesis techniques. This process with its fast pace in ascending and descending the temperature can produce meta-stable phase, un-equilibrium phase and products of tiny grains; therefore, superior properties are attainable compared to other synthesis techniques. This process with its fast pace in ascending and descending the temperature can produce meta-stable phase, un-equilibrium phase and products of tiny grains; therefore, superior properties are attainable compared to other synthesis techniques. This process with its fast pace in ascending and descending the temperature can produce meta-stable phase, un-equilibrium phase and products of tiny grains; therefore, superior properties are attainable compared to other synthesis techniques.

2.1. Preparation of ferrite

Ferrite powders were prepared by an amount of 25 g per batch from an exothermic reaction using mixtures of metal nitrates (purity: >99%, Aldrich) and urea ((NH2)2CO, purity: 99.5%, Aldrich). Reactants were directly mixed at an ‘equivalent stoichiometric ratio’ without adding water. Note that the ‘equivalent stoichiometric ratio’ is designated as the oxygen content of metallic nitrates that can be completely reacted to oxidize/consume urea exactly. The reactant mixture can easily absorb moisture from the air and become a slurry substance, since metallic nitrates possess hygroscopicity. This slurry mixture was homogenized and heated on a hot plate at ~230 °C to dehydrate until self-ignition was taken place. Then, the dried mixture was ignited at room temperature to start combustion reaction, giving rise to the evolution of a large volume of gases and producing a dry, loose, and voluminous ash. When complete combustion is assumed, the reaction equation can be expressed (greatly-simplified) as follows:

$$
(0.5 - x)\text{Ni(NO}_3)_2 + (0.5 - x)\text{Zn(NO}_3)_2 + 2x\text{M(NO}_3)_2 + 2\text{Fe(NO}_3)_3 + 6.67\text{CO(NH}_2)_2 \rightarrow
\text{Ni}_x\text{Zn}_{1-x}\text{M}_y\text{Fe}_2\text{O}_4 + 6.67\text{CO}_2 + 10\text{.67N}_2 + 13.34\text{H}_2\text{O}
$$

(1)

To understand the influences of heat treatment on grain size and magnetic properties, a portion of the as-synthesized ferrite powders was annealed at 500 °C and 900 °C for 1 h. For comparison, a commercial Ni0.5Zn0.5Fe2O4 (purity: 99%, average diameter: 1.5 μm, source: Core connector Co., Taiwan) manufactured by the conventional mixed oxide method was also used in the present study.

2.2. Characterization of ferrite

Phase formation of product was identified by using X-ray diffraction (XRD; SIEMENS D5000) with Cu Kα radiation (λ = 0.15418 nm). The crystallite size (D) of NiZn ferrite was calculated from the diffraction peak of the (3 1 1) plane from the XRD profile, in accordance with the Debye–Scherrer formula [20]:

$$
D = \frac{0.9\lambda}{\beta \cos \theta}
$$

(2)

where λ is the X-ray wavelength, β is the half-maximum breadth, and θ is the Bragg angle of the (3 1 1) plane. The morphological features and the electron diffraction patterns of the ferrite powders were imaged by transmission electronic microscope (TEM; Hitachi H-7100, Japan). Vibrating sample magnetometer (VSM; Toei, VSM-5) was used to determine the hysteresis loops of ferrite powders at room temperature.
2.3. Measurement of microwave-absorbing behavior for ferrite-TPU composite

The absorbing composite materials were prepared by molding and curing the mixture of ferrite powders and a TPU elastomer. TPU was used as a polymer matrix due to its good flexibility and high filler content. It becomes obvious that high filler content would enhance the complex permittivity of ferrite-polymer composite [21]. The mixing ratio of ferrite-to-TPU was fixed at 80% by weight. The testing specimens have a toroidal shape with both thickness being 1 mm and outer and inner diameters being 7.0 and 3.0 mm, respectively. The measurements of $\varepsilon'$, $\varepsilon''$, $\mu'$, and $\mu''$ versus frequency were made by coaxial reflection/transmission method using a Hewlett-Packard Network Analyzer (Model: HP8510C) in a 2–12 GHz frequency range.
The absorbing characteristics can be represented as the reflection loss (R.L.), to be described as [22]:

$$R.L. \text{ (dB)} = 20 \log_{10} \left| \frac{Z_{in} - 1}{Z_{in} + 1} \right|$$  \hspace{1cm} (3)

$$Z_{in} = \left( \frac{\varepsilon_r}{\mu_r} \right)^{1/2} \tanh \left[ j \left( \frac{2\pi fd}{c} \right) \left( \frac{\varepsilon_r}{\mu_r} \right)^{1/2} \right]$$  \hspace{1cm} (4)

where $Z_{in}$ is the normalized input impedance relating to the impedance in free space, $\varepsilon_r = \varepsilon' - j\varepsilon''$, $\mu_r = \mu' - j\mu''$ is the complex relative permeability and permittivity of the material, $d$ is the thickness of the absorber, and $C$ and $f$ are the velocity of light and the frequency of microwave in free space, respectively.

The impedance matching condition is given by $Z_{in} = 1$ to represent the perfect absorbing properties. The impedance matching condition is determined by the combinations of six parameters $\varepsilon'$, $\varepsilon''$, $\mu'$, $\mu''$, $f$ and $d$. Also, knowing the $\varepsilon_r$ and $\mu_r$, the R.L. value versus frequency can be evaluated at a specified thickness.

3. Results

3.1. Phase Identification

Fig. 2 shows the crystalline phases of as-synthesized undoped and doped ferrite powders. It is observed that only single spinel phase exists. In the doped ferrite cases, the dopants of Cu$^{2+}$, Co$^{2+}$, or Mg$^{2+}$ seem to dissolve/arrange in the spinel structure to fulfill the formation of single spinel phase. It is generally recognized that the vacancy sites of partial deprivation of Ni$^{2+}$ and Zn$^{2+}$ can be filled by these dopant ions arising from the facts that the ionic radii of Co$^{2+}$, Cu$^{2+}$ and Mg$^{2+}$ are actually $0.060 \text{ nm}$, $0.058 \text{ nm}$ and $0.057 \text{ nm}$, respectively, which are close to the ionic radii of Ni$^{2+}$ ($0.055 \text{ nm}$) and Zn$^{2+}$ ($0.060 \text{ nm}$). (These ionic radii mentioned above are simply for the case of coordination number (C.N.) = 4. When C.N. = 6, the ionic radii of Ni$^{2+}$, Zn$^{2+}$, Co$^{2+}$, Cu$^{2+}$ and Mg$^{2+}$ are 0.069 nm, 0.074 nm, 0.075 nm, 0.077 nm and 0.072 nm, respectively [23], which are nearly equal to each other.) Fig. 3 shows the more narrow peaks of NiZn ferrites after annealing at 500$^\circ$C and 900$^\circ$C for 1 h. It is expected that crystallite size after annealing will become larger due to grain growth. Table 1 depicts the result of the crystallite size determined by XRD. One can observe from this table that the grain size increases with respect to the increase of annealing temperature.

3.2. Morphology observation

The morphology of as-synthesized NiZn ferrite powders and the powder products annealed at 500$^\circ$C for 1 h with their corresponding electron diffraction patterns are shown in Fig. 4. The crystallite sizes were estimated to be $\sim 20 \text{ nm}$ for the as-synthesized powders and $\sim 35$–$45 \text{ nm}$ for the annealed...
ones in regard to which they are about the same sizes as the ones estimated by using XRD method. In addition, diffraction patterns indicate that the heat-treated powders have a higher degree of crystallinity than do the as-synthesized powders since their diffraction rings are sharper and brighter as compared with those of the powders without heat treatment.

3.3. Measurement of hysteresis loop

The hysteresis loop shown in Fig. 5 illustrates what are the real traces of the magnetic behavior of the as-synthesized NiZn ferrite as well as the ferrite samples that were annealed at 500 °C and 900 °C for 1 h. Table 1 presents the relevant data. It is interesting to recognize that the powders after annealing at 500 °C possess the largest coercive force ($H_c$), the largest hysteresis loop area ($A_H$) and the smallest remanence ($M_r$) than those of other samples, while the former two factors may lead to the largest hysteresis loss [24]. Moreover, the saturated magnetization ($M_s$) values of the calcined NiZn ferrites are smaller than that of the one without heat treatment.

![Fig. 4. TEM images of synthesized powders with corresponding diffraction patterns. (a) Without heat treatment, and (b) annealed at 500 °C for 1 h. (Taken at the same operation conditions).]

Table 1

<table>
<thead>
<tr>
<th>Specimen</th>
<th>$D$ (nm)</th>
<th>$H_c$ (Oe)</th>
<th>$M_s$ (emu/g)</th>
<th>$M_r$ (emu/g)</th>
<th>$A_H$ (kJ/m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Synthesized ferrite</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Without heat-treatment</td>
<td>25</td>
<td>52.22</td>
<td>44.24</td>
<td>3.421</td>
<td>41.25</td>
</tr>
<tr>
<td>Annealed at 500 °C/1 h</td>
<td>45</td>
<td>65.82</td>
<td>31.35</td>
<td>3.216</td>
<td>57.75</td>
</tr>
<tr>
<td>Annealed at 900 °C/1 h</td>
<td>80</td>
<td>28.01</td>
<td>38.82</td>
<td>1.489</td>
<td>34.17</td>
</tr>
<tr>
<td>Commercial ferrite</td>
<td>–</td>
<td>24.12</td>
<td>36.08</td>
<td>0.950</td>
<td>37.73</td>
</tr>
</tbody>
</table>

* Evaluated by the Debye–Scherrer formula.
The values of $d$ (i.e., the intersection point on positive $x$-axis) and $M_r$ (i.e., the intercept on positive $y$-axis) for each specimen can be observed.

Fig. 6. Room-temperature hysteresis loops of synthesized doped- and undoped NiZn ferrite-TPU composites. The matching frequency ($f_m$) is equal to 3.16 GHz in the lower-frequency region and it is equal to 9.43 GHz in the higher-frequency region. The corresponding values of matching thickness ($d_m$) are 5.92 mm and 2.13 mm, respectively. Table 3 lists the data of absorption characteristics for the absorbing composites fabricated from the commercial NiZn ferrite, as-synthesized and annealed at 500 °C and 900 °C for 1 h. It is clear that these NiZn ferrite-TPU composites can be considered as a microwave-absorbing material in the 2–4 GHz lower-frequency range and in the 9–10 GHz higher-frequency range. In particular, the NiZn ferrite after annealing at 500 °C for 1 h exhibits the largest reflection loss and the widest bandwidth than those obtained from other specimens. This phenomenon, coupled with the results presented in Table 1, suggests that the crystallite size of NiZn ferrite has significant effects on magnetic properties and microwave-absorbing characteristics.

Table 4 shows the absorption efficiency for the undoped, Co-doped, Mg-doped, and Cu-doped NiZn ferrite-TPU composites to be obtained by taking the specified thickness of 2 mm and 5 mm, respectively. It shows that the reflection loss of these composites could be designed to be more negative than −20 dB in the frequency range of 2–12 GHz. In addition, it is evident that the doped ferrite-containing composites have much more effective electromagnetic absorb-
Table 2: Detail data for hysteresis loops shown in Fig. 4

<table>
<thead>
<tr>
<th>Specimen</th>
<th>$H_c$ (Oe)</th>
<th>$M_s$ (emu/g)</th>
<th>$M_r$ (emu/g)</th>
<th>$A_H$ (kJ/m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Doped ferrite</td>
<td>Ni₀.₄₅ Zn₀.₄₅ Co₀.₁ Fe₂O₄</td>
<td>161.4</td>
<td>49.30</td>
<td>10.04</td>
</tr>
<tr>
<td></td>
<td>Ni₀.₄₅ Zn₀.₄₅ Cu₀.₁ Fe₂O₄</td>
<td>112.5</td>
<td>44.53</td>
<td>7.431</td>
</tr>
<tr>
<td></td>
<td>Ni₀.₄₅ Zn₀.₄₅ Mg₀.₁ Fe₂O₄</td>
<td>112.2</td>
<td>42.85</td>
<td>6.907</td>
</tr>
<tr>
<td>Undoped ferrite (Ni₀.₅ Zn₀.₅ Fe₂O₄)</td>
<td>65.82</td>
<td>31.35</td>
<td>3.216</td>
<td>57.75</td>
</tr>
</tbody>
</table>

* As-synthesized ferrites calcined at 500°C for 1 h.

Discussion

By using the combustion synthesis method and annealing process, we were able to fabricate NiZn-ferrite powders with particle size ranging from ~20 nm to a size approximately 80 nm. The commercial Ni₀.₅ Zn₀.₅ Fe₂O₄ powder with microscale size was also fabricated. From Fig. 4 and Table 3, it is found that the crystallite size obtained at calcinations temperature of 500°C, which is ~35–45 nm, has better reflection loss and bandwidth than those acquired from greater particle size (in micro-sized range) or as-synthesized one (<25 nm). Recent report [25] claims that a critical particle size becomes available as transited from mono-magnetic-domain to multi-magnetic-domain to be close to 40 nm. In this transition stage, both domain wall motion and spin rotation are in operation us-

![Fig. 7. Permittivity and permeability spectra of Ni₀.₅ Zn₀.₅ Fe₂O₄-TPU composites. (a) $\varepsilon'$, (b) $\varepsilon''$, (c) $\mu'$, and (d) $\mu''$.](image-url)

(a) As-synthesized ferrite without heat treatment, (b) synthesized ferrite annealed at 500°C for 1 h, (c) synthesized ferrite annealed at 900°C for 1 h, and (d) commercial ferrite.
Fig. 8. Permittivity and permeability spectra of doped- and undoped NiZn ferrite-TPU composites. (a) $\varepsilon'$, (b) $\varepsilon''$, (c) $\mu'$, and (d) $\mu''$. (□) Undoped, (♦) Co-doped, (♦) Cu-doped, and (⋆) Mg-doped. (All of these synthesized ferrites were annealed at 500°C for 1 h).

Fig. 9. Absorption characteristics of the Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$-TPU composite with maximum attenuation. (All of the synthesized ferrite was annealed at 500°C for 1 h.)

Table 3. Relationship between matching frequency and matching thickness in Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$-TPU composites

<table>
<thead>
<tr>
<th>Specimen</th>
<th>$f_m$ (GHz)</th>
<th>$d_m$ (mm)</th>
<th>R.L. (dB)</th>
<th>Bandwidth$^a$ (GHz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Synthesized ferrite</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Without heat treatment</td>
<td>9.15</td>
<td>3.07</td>
<td>-32.38</td>
<td>0.74</td>
</tr>
<tr>
<td>Annealed at 500°C/1h</td>
<td>9.43</td>
<td>2.13</td>
<td>-43.71</td>
<td>1.10</td>
</tr>
<tr>
<td>Annealed at 900°C/1h</td>
<td>8.89</td>
<td>3.42</td>
<td>-29.47</td>
<td>0.69</td>
</tr>
<tr>
<td>Commercial ferrite</td>
<td>9.02</td>
<td>3.23</td>
<td>-31.81</td>
<td>0.70</td>
</tr>
<tr>
<td></td>
<td>2.97</td>
<td>5.62</td>
<td>-33.46</td>
<td>0.79</td>
</tr>
</tbody>
</table>

$^a$ For R.L. $\leq$20dB.
to large hysteresis attenuation and absorbing behavior. Our experimental results agree with this perspective.

On the other hand, when the M$^{2+}$ ion (M=Co, Cu, or Mg) substitutions are introduced into the sublattices in the reversed NiZn spinel ferrite, it may occupy the octahedral sites in replacing the Zn$^{2+}$ or Ni$^{2+}$ ions due to their nearly the same radii. The strength of the superexchange interaction can be reduced whereas the magnetic moments can be improved, resulting in an increase in the spontaneous magnetization [27]. Some researches have been made also to verify that not only can the saturation magnetization (M$_s$) and coercive force (H$_C$) of NiZn ferrites be enhanced by substituting a portion of Zn$^{2+}$ or Ni$^{2+}$ ions by divalent metal ions such as cobalt, but also the initial permeability [6–9,28]. In this work, for the Co-doped, Cu-doped, and Mg-doped NiZn ferrite, the permeability and the hysteresis loop can be modified due to the presence of these dopants, which is in agreement with the statement mentioned above (see Table 2 and Fig. 6). The further improved magnetic properties of these doped ferrites were also reported in Refs. [6–9,26], and thereby it would be instructive to suggest that the doped-ferrite compositions possess better absorbing characteristics when compared with the undoped one. This opinion may be verified using the data listed in Table 4.

In summary, in this work, the experimental results indicate that the grain size of the NiZn ferrites and the presence of the dopant affect the microwave-absorbing behavior of the ferrite-TPU composite. Therefore, the improved reflection losses were thought to be related to enhanced permeability, larger coercive force, and large hysteresis loop. These results can be attributed to be from the domain wall motion and spontaneous magnetization. Further investigation for the effects of both ferrite and dopant content on the relationship between the electromagnetic characteristics of nano-sized ferrite composites and their microwave-absorbing properties are underway and we will soon disclose where we stand.

5. Conclusion

In this study, we have carried out experiments to demonstrate the dependence of particle size of NiZn ferrite on the reflection loss of ferrite-TPU composite by using combustion synthesized powders (20–80 nm) and commercial micro-sized powders. It is found that nanocrystallite of NiZn ferrite around 35–45 nm exhibit higher reflection loss than both those of micro-sized powders and those with size less than 25 nm. In addition, the Co-doped, Mg-doped, and Cu-doped NiZn ferrite-TPU composites have more effective absorption effect than the undoped one. These composites could be designed to be more negative than –20 dB in a frequency range of 2–12 GHz to be able to become promising materials for microwave-absorbing application.

Acknowledgements

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References


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Table 4

Reflection loss of composites made from synthesized doped and undoped ferrite powders annealed at 500°C for 1 h

<table>
<thead>
<tr>
<th>Specimen</th>
<th>R.L. (dB)</th>
<th>Location of maximum R.L. (GHz)</th>
<th>Band width*(GHz)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$d = 2$ mm</td>
<td>$d = 5$ mm</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$d = 2$ mm</td>
<td>$d = 5$ mm</td>
<td></td>
</tr>
<tr>
<td>Co-doped NiZn ferrite</td>
<td>–30.74</td>
<td>–42.51</td>
<td>0.34</td>
</tr>
<tr>
<td>Cu-doped NiZn ferrite</td>
<td>–27.61</td>
<td>–37.07</td>
<td>0.21</td>
</tr>
<tr>
<td>Mg-doped NiZn ferrite</td>
<td>–23.41</td>
<td>–29.32</td>
<td>0.12</td>
</tr>
<tr>
<td>Undoped NiZn ferrite</td>
<td>–21.52</td>
<td>–24.34</td>
<td>0.10</td>
</tr>
</tbody>
</table>

* For R.L. ≤20 dB.